The Optical Basicity and Fe^{2+} - Fe^{3+} Redox in Oxyacid Salt Systems

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The optical basicity (Λ ; Pb^{2+} as probe ion) of various oxide glass systems has been measured to establish the new basicity scale of oxyacid salt melts. Best conditions of glassy fragments to measure Λ were determined. Problems in establishing the new basicity scale using Λ -values are discussed, and also relation between Λ and Fe^{2+} - Fe^{3+} redox equation is discussed in terms of Fe^{3+} -constitution. Λ has the possibility of showing the Lewis and new scale of basicity in these melts.

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I. Introduction

The basicity of oxyacid salt melts is one of the most important parameters in the metallurgical process, especially in smelting slag and continuous casting flux. The value of Basic oxide / Acidic oxide, like CaO/SiO_2 , $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$, has been applied for the basicity of these melts. But recently various systems of these melts have been used, for example ferrite type slag in Mitsubishi Process⁽¹⁾⁽²⁾, and soda-metallurgy in steel making⁽³⁾, so that a new scale of basicity in these melts may be necessary. For this purpose many works have been conducted to measure the basicity of oxyacid salt melts using various methods, i.e., e.m.f.-measurement in oxygen concentration cell⁽⁴⁾⁽⁵⁾, CO_2 absorption into the melts⁽⁶⁾, and determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the melts⁽⁷⁾⁽⁸⁾. None of these basicities, however, was effective to apply to various oxyacid systems in the same scale of basicity.

The optical basicity derived from the nephelauxetic effect of Pb^{2+} -probe ion in quenched oxyacid salts has the possibility of showing a new scale of basicity in any melts⁽⁹⁾. In the present work, the experimental technique for measuring the optical basicity of quenched oxyacid salts is presented, and the usefulness

of the optical basicity scale is discussed. Fe-redox equation in oxyacid salt melts is also considered in terms of the optical basicity of these melts.

II. Principle and Experimental Procedure

1. Principle of optical basicity⁽⁹⁾⁽¹⁰⁾

The optical basicity is derived and calculated from the peak shift of s-p spectra in the probe ion caused by the nephelauxetic effect.

The probe ions, Tl^+ , Pb^{2+} and Bi^{3+} used for optical basicity are p-block metal ions. The electronic configuration of these metal ions is $d^{10}s^2$ -type, and has a sharp absorption band in the ultraviolet region. In case of Pb^{2+} the nephelauxetic effect is described as shown in Fig. 1. Some of the electron density is located between the inner electron core of the metal ion and its 6s orbital. Pb^{2+} has a pair of electrons in the 6s orbital; much of the positive pull of the nucleus is screened by the inner electron core ((a) in Fig. 1). The electron density donated by the oxygens (in this study), fluorines, chlorines etc. serves to increase this screening and this in turn allows 6s electron to escape more easily to 6p level. Electron donation by the oxygen to the probe ion, therefore, brings out a reduction in the 6s-6p energy gap ((b) in Fig. 1), and a shift in frequency in the UV absorption band, compared with the free Pb^{2+} ion ((a) in Fig. 1). It is called the nephelauxetic effect.

From this effect, the number of oxygen ion providing a pair of electrons to Pb^{2+} in

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Fig. 1 Schematic diagram of (a) free Pb^{2+} ion, and (b) Pb^{2+} ion after receiving negative charge from neighbouring oxygen ions.

quenched oxyacid salts can be determined by the wave number shift in the s-p spectra of Pb^{2+} . The number of oxygen ions is related to the oxygen activity of oxyacid salts and will become to be a new scale of basicity. This basicity is called the optical basicity. The wave number shift in the s-p spectra is normalized, and the optical basicity is defined by the following equation,

$$\Lambda = \frac{(v_{\text{free ion}} - v_{\text{glass}})}{(v_{\text{free ion}} - v_{\text{O}^{2-}})}, \quad (1)$$

where Λ is the optical basicity (0–1), and $v_{\text{free ion}}$ is the peak wave number in s-p spectra of free probe ion, to which a pair of electrons is not donated by a ligand. $v_{\text{free ion}}$ may be calculated by extrapolation of the linear relationship between measured spectroscopic shifts and orbital expansion parameters for various ligand environments. In this study $v_{\text{free ion}}$ (Pb^{2+}) is $6.07 \times 10^6 \text{ m}^{-1}$ (60700 cm^{-1}). $v_{\text{O}^{2-}}$ is the peak wave number of the s-p spectra of the Pb^{2+} ion which exists in free O^{2-} . For Pb^{2+} a value for $v_{\text{O}^{2-}}$ of $2.97 \times 10^6 \text{ m}^{-1}$ (29700 cm^{-1}) is taken from comparison with data for CaO. For the Pb^{2+} probe ion Λ can be calculated by the following equation.

$$\Lambda = \frac{(6.07 - v_{\text{glass}})}{3.10}. \quad (2)$$

v_{glass} is the peak wave number in s-p spectra of Pb^{2+} ion, which exists in quenched oxyacid salt. More detailed descriptions are given on the references⁽⁹⁾⁽¹⁰⁾.

2. Experimental procedure

All samples were prepared from special grade carbonate and oxide reagents. It must be confirmed that the reagent contains no Pb as impurity. The PbO reagent used as probe was added about $4 \times 10^{-2} \text{ wt\% Pb}$, and mixed samples were melted in a Pt-crucible for uniform liquid at 1273 K for the alkali oxide-borate system, 1473 K for the alkali earth oxide-borate system, 1573 K for the phosphate and alkali oxide-silicate systems and 1873 K for the CaO– SiO_2 system, respectively and then quenched to glassy samples. Glasses were annealed enough to prevent the breakage during cutting of the sample into a piece of 0.2 mm in thickness for polishing. v_{glass} was measured by a spectrometer (Hitachi EPS-3T-type), and Λ was calculated by eq. (2).

The samples for $\text{Fe}^{2+}/\text{Fe}^{3+}$ measurement were also prepared from special grade carbonate and oxide reagents. Mixed samples containing 0.5 mol% Fe_2O_3 were melted in a Pt-crucible for about 21.6 ks enough to equilibrate with oxygen in air and quenched to be glassy samples. A volumetric method has been used

for the determination of small amounts of Fe^{2+} in glass on the basis of reaction with ICl , which was developed for the determination of As^{3+} in glass by Hey⁽¹¹⁾ and Paul⁽¹²⁾. The sample is dissolved in HF solution and then ICl is added. The iodine liberated by the following chemical reaction is titrated with $\text{M}/1000$ potassium iodate solution.

The method is accurate and reproducible within $\pm 2.5\%$. Total amounts of Fe is determined by the conventional permanganate titration method. P_2O_5 is determined by the volumetric method⁽¹³⁾, because it is likely to vaporize.

III. Results

1. Conditions for the optical basicity measurement

Further details on these conditions have never been seen in the literature. Some preliminary experiments were carried out to

determine the optimum conditions for the optical basicity measurement.

Figure 2 shows the effect of PbO content on the spectra of Pb_{s-p} in Na_2O (40 mol%)- SiO_2 glass with the same thickness. PbO contents are 4×10^{-4} kg, 2×10^{-4} kg, 1×10^{-4} kg and 5×10^{-5} kg per 1 kg sample, respectively. It is clear that the peak position of these spectra is not changed with PbO content. The peak position of the spectrum in which PbO content is 4×10^{-4} kg can be seen independently from the spectrum of SiO_2 in the lower wave length region, so the wave number of the peak position can be determined accurately. The peak position of the spectrum in which PbO content was more than 8×10^{-4} kg could not be determined because of the over scale of the spectra in Pb_{s-p} . Then the most suitable PbO content in this study is 4×10^{-4} kg per 1 kg sample. The optimum thickness of sample is 0.2–0.4 mm, and there is no change in the peak position with the change of thickness. Samples were annealed for 18–36 ks below the temperature T_g (750–1100 K) to avoid the breakout

Fig. 2 Effect of PbO content on Pb_{s-p} spectra shift.

Fig. 3 Effect of composition on Pb_{s-p} spectra shift.

at cutting. It was also revealed that there was no change in the peak position with the change of annealing period. Figure 3 shows the effect of composition on $\text{Pb}_{\text{s-p}}$ spectra shift, where the absorption peak markedly shifts with the change in CaO content. That is, the peak position was found to shift only with the change in composition in these experimental conditions. Optical basicity thus obtained can be in error by as much as 0.1 %.

2. Results of optical basicity measurement

The relation between optical basicity (Λ) and composition in silicate glasses is shown in Fig. 4. Λ of both the Li_2O – SiO_2 and Na_2O – SiO_2 systems change linearly with composition. The results indicate that the Na_2O system is more basic than the Li_2O system as expected from the oxygen-ion attraction and electronegativity of Na^+ and Li^+ . Λ in the CaO –

Fig. 4 Relation between composition and optical basicity in silicate systems.

Fig. 5 Relation between composition and optical basicity in phosphate systems.

SiO_2 system, however, changes non-linearly. It may be possible to discuss the structure change in these glasses according to the change in optical basicity.

Figure 5 shows the relation between Λ and composition of phosphate glasses. Λ of both the Na_2O – P_2O_5 and CaO – P_2O_5 systems change linearly with composition, showing higher basicity for the Na_2O system than for the CaO system. Λ of the silicate system (Fig. 4) changes in the range of 0.53 to 0.62, whereas for the phosphate system it changes in the range of 0.40 to 0.51. As one would expect, the phosphate system is considered more acidic than the silicate system.

Figure 6 shows the optical basicity as a function of composition in the alkali-earth oxide-borate systems. In these systems, the optical basicity will increase with increasing content of alkali-earth oxide as in other systems, and

Fig. 6 Relation between composition and optical basicity in borate systems.

Fig. 7 Relation between composition and optical basicity, relative oxygen ion activities in borate systems.

its value will be expected from oxygen-ion attraction or electronegativity of basic oxides. Figure 7 shows Λ in the alkali oxide-borate system together with the experimental values obtained by other authors about the relative oxygen ion activity⁽¹⁴⁾ calculated from the e.m.f. of concentration cell of these melts. As shown in Fig. 7, the acid-base relation between the $K_2O-B_2O_3$ system and the $Na_2O-B_2O_3$ system is reversed at the composition of 22 mol% K_2O or Na_2O . At the same composition, the relative oxygen activity of both the systems is also reversed, as seen in the figure. It can be said that Λ of quenched slags is correlated to the basicity of slag melts. In the range over 15 mol% alkali-oxide, the degree of increasing Λ is greater than that of lower content. This tendency seems to be correlated to the change in the oxygen coordination number of B^{3+} ion⁽¹⁵⁾.

Figure 8 shows the observed values of Λ (solid lines) and the theoretical values (dashed lines) at the composition range of 20 to 50 mol% alkali or alkali-earth oxides. The theoretical values are calculated from the equation proposed by Duffy, *et al.* which takes into account the electronegativity, valency and cation/ O^{2-} radius ratio. Figure 4 indicates that in the phosphate and silicate systems the observed values Λ are a little smaller than the theoretical values, that is, the observed optical basicity is more acidic. In the borate system, on the contrary, Λ of the observed values are larger than that of the theoretical values. In the germanate system, the difference between

Fig. 8 Observed range of optical basicities in silicate, borate, phosphate and germanate systems.

both values is large. The theoretical value of the GeO_2 system appeared as strongly acidic compared with the experimental values, because the change in the oxygen coordination number of Ge^{4+} ion from 4 to 6⁽¹⁶⁾ is not considered during the calculation. In the B_2O_3 system, the measured value is consistent with the theoretical value because of the consideration of the change in the oxygen coordination number. These results show that the change in the oxygen coordination number of Ge^{4+} or B^{3+} ion may be discussed with the measurement of the optical basicity in detail.

3. Fe^{2+}/Fe^{3+} ratio

Figure 9 shows Fe^{2+}/Fe^{3+} ratio of glasses quenched from the melts at 1573 K. Fe^{2+}/Fe^{3+} ratio decreases with increasing Na_2O content in the Na_2O-SiO_2 and $Na_2O-P_2O_5$ systems, which is called O-type redox. In the $CaO-P_2O_5$ systems, however, Fe^{2+}/Fe^{3+} ratio increases with increasing CaO content, which is called R-type redox. Such tendency is observed in the glasses quenched from other temperatures. These values of Fe^{2+}/Fe^{3+} ratio and the tendency are consistent with the studies of other investigators⁽⁷⁾⁽⁸⁾⁽¹⁷⁾. In the range of 25 to 30 mol% Na_2O in the Na_2O-SiO_2 system, Fe^{2+}/Fe^{3+} ratio seems to have the maximum value only when the Pt crucible is used. This condition involved in such Na_2O range was not discussed here, because Paul *et al.*⁽⁷⁾ provided the idea about the redox equation that the Pt crucible used for a con-

Fig. 9 Relation between Fe^{2+}/Fe^{3+} ratio and composition.

tainer might participate in the redox reaction.

IV. Discussion

1. Optical basicity and Fe^{2+} – Fe^{3+} redox equilibrium

Figure 10 shows the relation between the optical basicity and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio from Fig. 9. The points in the parentheses belong to the compositions which are considered to be affected by the $\text{Pt}^{(4)}$ crucible. From Fig. 10 $\log(\text{Fe}^{2+}/\text{Fe}^{3+})$ takes a maximum value at about 0.5 in Λ . When Λ is more basic than 0.5 ($\Lambda > 0.5$), $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreases with the increase of basicity, and when Λ is more acidic than 0.5 ($\Lambda < 0.5$), it increases with the increase of basicity.

The equations of redox equilibrium involving transition metal oxide in the melts are generally divided into two types, that is, O-type and R-type⁽¹⁷⁾⁽¹⁸⁾⁽¹⁹⁾. For Fe^{2+} – Fe^{3+} redox, the equation is described as follows;

when $n > \frac{1}{2}$, for example $n=3$, eq. (3) is

and when $n < \frac{1}{2}$, for example $n=0$

Equations (4) and (5) are called as O-type and R-type, respectively, and the dependence of the value of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio upon O^{2-} (oxygen ion activity) in eq. (4) is opposite to that in eq. (5). It will depend upon the type of anion like Fe^{3+} or FeO_n^{3-2n} whether the redox equation is either O-type or R-type as seen in eqs. (4) and (5). In the region of strong acid like below 0.5 of Λ (CaO – P_2O_5 system), Fe^{3+} is considered to be present as Fe^{3+} cation, and the redox equation is like (5). In the region of strong base over 0.5 of Λ , however, Fe^{3+} takes complex anion like FeO_n^{3-2n} , and the redox equation is O-type expressed in eq. (4).

The authors⁽²⁰⁾ discussed about the constitutions of Fe^{3+} complex anion from measurements of the isomer shifts (δ) of Mössbauer

Fig. 10 Relation between $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and optical basicity.

Fig. 11 Relation between optical basicity and isomer shift of Fe^{3+} in Mössbauer effect. (δ ; ref. N.P.)

spectra for Fe^{3+} in the Na_2O – SiO_2 and CaO – SiO_2 glass systems. Figure 11 shows the relation between the optical basicity (Λ) and isomer shift (δ) of Fe^{3+} from the report⁽²⁰⁾, where the samples for the measurement of δ contain 10 mol% Fe_2O_3 . The value of δ reflects the bonding between Fe^{3+} – O^{2-} , that is, the larger the value of δ becomes, the larger the ionic property of bonding is. On the contrary the smaller the value of δ becomes, the stronger the covalent bonding is⁽²¹⁾. Figure 11 shows

good linearity between Λ and δ , and like the previous report⁽²⁰⁾, when Λ of the system is large, δ is small and the covalent bonding between Fe^{3+} and O^{2-} is stronger. When Λ of the system is small, δ is large and the ionic bonding between them is stronger.

For the sample of $\text{CaO} \cdot \text{P}_2\text{O}_5$ which is the strongest acid in this study, δ is 0.73 and Fe^{3+} is assumed to be strong ionic, resulting in the type of Fe^{3+} cation. The Fe^{2+} – Fe^{3+} redox equation in CaO – P_2O_5 system in which Λ is below 0.5 as seen in Fig. 10 is considered as R-type as eq. (5). In the silicate system in which Λ is mostly over 0.55, δ is below 0.6 and Fe^{3+} is assumed to have the strong covalent bonding and to be present as oxygen complex anion like FeO_n^{3-2n} . The redox equation in the Na_2O – SiO_2 system will be described as O-type as eq. (4).

On the other hand, δ of Fe^{3+} ion in $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ is 0.71 and the bond between Fe^{3+} and O^{2-} is considered to be strong ionic, but the redox equation is O-type like the Na_2O – SiO_2 system from Fig. 9. The authors⁽²⁰⁾ have discussed about the presence of FeO^+ ($\text{Fe}_2\text{O}_3 \rightarrow 2\text{FeO}^+ + \text{O}^{2-}$) as one of the existing states of incompletely dissociated Fe_2O_3 . Yokokawa *et al.*⁽¹⁷⁾ proposed the ionic species of $\text{FeO}_{0.7}^{+1.6}$ as one of constitutions of Fe^{3+} from the investigation of Fe^{2+} – Fe^{3+} redox equation in the Na_2O – P_2O_5 system. In the Na_2O – P_2O_5 system ($\Lambda \cong 0.50 \sim 0.55$), the following eq. (6) will be considered.

There appears to be good correlation among the measured optical basicity, $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and δ of Mössbauer spectra of Fe^{3+} .

2. Problems found in the optical basicity

Some problems should be brought into consideration when the basicity of molten oxide is estimated from the results of optical basicity measurements for the quenched oxide glasses. That is,

- (1) the site selectivity of probe ion⁽⁹⁾⁽²²⁾⁽²³⁾,
- (2) the correlation of basicity between glass and melt,
- (3) the impossibility of measuring the

optical basicity of opaque or colored glasses. Eastal⁽²²⁾ and Duffy⁽⁹⁾⁽²³⁾ discussed about the problem (1). From the results of the present study using Pb^{2+} , Bi^{3+} and Tl^+ as probe ions, the change in peak shift is the largest with the composition change for using Pb^{2+} ion, and consequently high accuracy of measurements will be expected. The theoretical or calculated value of optical basicity is in good agreement with the measured value in the silicate, phosphate and borate systems (Fig. 8). Also the optical basicity is in good agreement with the estimation from oxygen-ion attraction as mentioned in IV-1. All these results will recommend a use of Pb^{2+} ion for the measurements of optical basicity.

For the problem (2), the change in Λ of quenched glass is assumed to reflect the change in relative oxygen ion activity in melt, that is, the change in the basicity, because the change in Λ in borate glasses is similar to the change in the relative oxygen ion activity of the molten borate system, as shown in Fig. 7.

For the problem (3), it is possible for the opaque or colored glass to provide the basicity normalized in 0 to 1 by establishing the calibration lines showing the relationship between the optical basicity (Λ) and the redox equilibria of $\text{Fe}^{2+}/\text{Fe}^{3+}$ or the isomer shift (δ) of Mössbauer spectra of Fe^{3+} .

V. Conclusions

The measuring methods of optical basicity for quenched oxyacid salt glasses are established, and the problems involved in this process are described with the methods of solution. The possibility to express the basicity of oxyacid salt melts as a unified scale like pH scale in the aqueous solutions by using the optical basicity is investigated with the discussion on the relationship between optical basicity and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox equation.

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